

LA-UR-15-27331

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Title: Extractant Design by Covalency

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Intended for: Report

Issued: 2016-01-21 (rev.1)

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Extractant Design by Covalency, FT-15LA030408

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Importance of Work and Context to DOE-NE Mission: This project aims to provide an electronic structure-to-function understanding of extractants for actinide selective separation processes. The research entails a multi-disciplinary approach that integrates chemical syntheses, structural determination, K-edge X-ray Absorption Spectroscopy (XAS), and Density Functional Theory (DFT) calculations. In FY15, the project reached the final stage of testing the extraction performance of a new ligand design and preparing an americium-extractant complex for analysis.

Summary of Research Accomplishments and FY15 Results: Two key advances were successfully completed: 1) Based upon the previous deciphering of electronic structure from sulfur K-edge XAS data, a new extractant design proposed by a ‘rational’ chemical bonding knowledge driven process (as opposed to the traditional trial and error approach) was synthesized on a multi-gram scale and predicted to be actinide selective; solvent extraction tests confirmed this hypothesis to be correct. 2) The first americium-dithiophosphinate extractant complex was isolated and structurally characterized. This is expected to be a vital step in demonstrating direct spectroscopic proof of the enhanced covalency in Am-S versus Ln-S bonds that is hypothesized to be responsible for observed Am/Ln separation factors in separation studies.

Research in previous years had focused on probing the sulfur K-edge in dithiophosphinate extractant molecules, and uncovered clear electronic structure differences that correlate to differences in observed Am/Ln separation factors. It appeared that the steric repulsion imparted by the *o*-CF₃ substituents causes the phenyl rings to twist with respect to each other. A consequence of this geometrical arrangement (which is different from other less selective dithiophosphinate extractants) is enhanced orbital mixing in the highly actinide-selective [S₂P(*o*-CF₃C₆H₄)₂]⁻ extractant and this facilitates increased negative charge delocalization, and therefore provides a rational basis from which to propose new extractant designs/modifications. Specifically, the hypothesis was that if the two aryl rings could be chemically tethered through a carbon-chain linker to ‘lock-in’ the ring twist then orbital mixing and negative charge delocalization will be enhanced, which should render the molecule highly actinide selective on the basis of sulfur K-edge XAS analysis and DFT predictions. In FY14, a new ‘ring-tethered extractant design, [S₂P(C₁₂H₈)₂]⁻ (**1**), was developed but suffered from poor solubility in organic diluents. This problem was overcome in FY15 by installation of tert-butyl groups on the phenyl rings to form new extractant **2** (Figure 1) on a multi-gram scale.

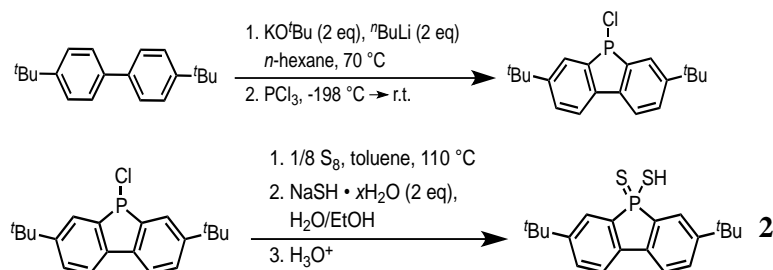
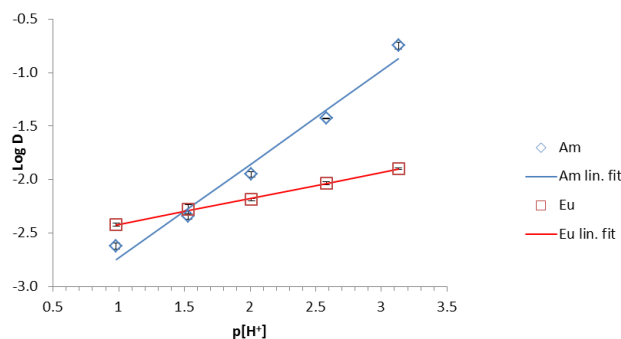


Figure 1. Synthetic steps for the preparation of new extractant design **2** in gram quantities.

Biphasic solvent extraction separation measurements performed at INL confirmed that the new ‘rational’ design process developed by this project, based upon electronic structure properties, does indeed result in a new extractant design that exhibits Am(III) versus Ln(III) selectivity. The chosen organic diluent was the sulfone ‘FS-13’ to be consistent with the Separation Factor (SF) measurements in

the literature for other dithiophosphinates. At a pH value of 3, and an extractant (**2**) concentration of 0.05 M in sulfone FS-13 organic diluent the measured SF was 14 (Figure 2). While the SF value was much lower than the *o*-CF₃ substituted diphenyldithiophosphinate, it is higher than the unsubstituted diphenyldithiophosphinate, [S₂PPh₂]¹⁻, and demonstrates the principle that tethering the aryl rings together to restrict geometric rotation allows a rational design process whereby the desired electronic structure and orbital mixing can be ‘dialed in’ to achieve actinide selectivity. Other factors such as solubility may account for why the SF is not as high as expected and further research may allow optimization of the SF.

Figure 2. Plot of distribution ratios (between the organic and aqueous phase - logD) against pH of the



aqueous phase, for the ‘rationally-designed’ tethered extractant **2**.

In FY15 the coordination chemistry of the new extractant **2** was investigated with lanthanides and actinides in order to begin to gain an understanding of the complexes and bonding properties that may be formed in separations. Significantly, the first complex of a dithiophosphinate with americium(III) was isolated and structurally characterized (Figure 3). This result provides the basis for electronic structure calculations and covalency interpretation of sulfur K-edge XAS measurements, which are anticipated to reveal the first direct experimental evidence of increased metal-ligand orbital mixing in the Am-S versus Ln-S bond. Approval to ship high specific-activity ²⁴³Am-containing samples to the Stanford Synchrotron Radiation Laboratory for XAS measurements was obtained after years of safety and containment testing with lanthanide, uranium, neptunium and plutonium samples. An initial Am-dithiophosphinate sample was shipped to the beamline and tested, but future measurements on higher purity samples will be needed to provide sufficient data for covalency interpretation.

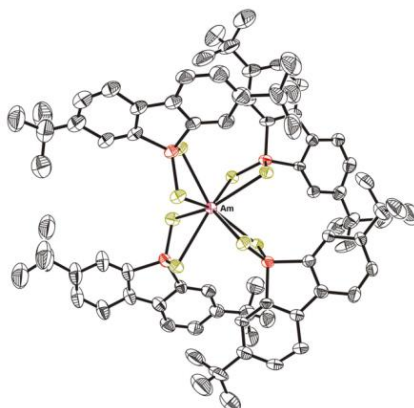


Figure 3. Solid-state structure of Am^{III}[S₂P(C₁₂H₆¹Bu₂)]₄¹⁻, an anionic tetrakis complex of Am(III) with **2**.

In summary, the project has demonstrated that K-edge XAS is a tool that can be successfully utilized to correlate electronic structure to separation behavior and rationally propose new actinide selective ligand designs.